U. S. NAVAL SUBMARINE MEDICAL CENTER

Submarine Base, Groton, Conn.

REPORT NUMBER 629

SOME CONSIDERATIONS IN ESTABLISHING PURITY STANDARDS FOR CARBON MONOXIDE IN THE BREATHING GAS OF DIVERS

by

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Bureau of Medicine and Surgery, Navy Department
Research Work Unit M4306.02-2110B.01

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NAVAL SUBMARINE MEDICAL CENTER REPORT NO. 629

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SUMMARY PAGE

THE PROBLEM

To summarize currently established standards of gas purity in breathing mixtures for divers, especially as it concerns carbon monoxide, and to discuss in depth some of the newer considerations related to hyperbaric exposure.

THE FINDINGS

Establishment of a single standard is not practical for universal use. The length of exposure time and many other circumstances must be taken into consideration. This paper outlines the parameters for which standards have been documented and suggests several other areas for which information must be developed.

APPLICATIONS

The findings of this paper are important for all those concerned with breathing media for divers, ---whether recreational divers, hard-hat divers, ship's hull inspectors, members of underwater demolition teams, or aquatic habitat excursion divers.

ADMINISTRATIVE INFORMATION

This investigation was conducted as a part of Bureau of Medicine and Surgery Research Work Unit M4306.02-2110B - Vertical Excursion Diving Limits in Air and Mixed Gas Human Saturation Diving. The present report is No. 1 on this Work Unit. The manuscript was approved for publication on 12 June 1970, and designated as Submarine Medical Research Laboratory Report No. 629. The material will subsequently be presented to a Symposium on Purity Standards for Divers, 9 July 1970, at Battelle Memorial Institute, Columbus, O.

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ABSTRACT

The literature on carbon monoxide toxicity is voluminous and growing. In environments of one atmosphere, the short-term effects of various breathing gas and blood levels are fairly well defined as a function of exposure time. There is, however, incomplete data on which to base extrapolation of these limits to the hyperbaric environments or to evaluate the existence of long-term effects. The implications of elevated oxygen partial pressures, incomplete carbon dioxide removal, isobaric increased partial pressure of the contaminant, and body metabolism sources of carbon monoxide are only poorly understood. This paper briefly reviews the rationale for the currently established standards, and discusses in depth some of the new considerations related to hyperbaric exposure.

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INTRODUCTION

For over a century, man, in his adaptation to the products of the industrial revolution, has had to deal with carbon monoxide as an entity of a toxic nature. This specter of incomplete combustion has been found in the home, the factory, the city street, the cigarette smoker with the result that the question has been raised in many settings as to what is a tolerable level of exposure. In most cases, a tolerance level has been promulgated by test, or educated guess. The physician who was called to care for the unconscious patient wished to be able to prognosticate from the carboxyhemoglobin level. The industrial hygienist wanted to know what was "safe" for an eight-hour day, forty-hour week exposure. Later, the voice of the community at large was heard. It posed the question of extended exposures, lifetime's tolerances for citizens young, old, healthy and ill, and the hazards of congested streets and poorly ventilated tunnels (see Table I). As the vista of carbon monoxide contamination expanded, the diving community finally became concerned, and it too desired to have the toxic limits evaluated for its own particular circumstances.

Table I. - Carbon Monoxide and Threshold Limits

Type of Limit	Year	Atmosphere Level	Reference
Occupational	1959	100 ppm	ACGIH 1959[2]
Occupational	1965	50 ppm	Industrial Hyg. Guides 1965[13]
Community	1969	20 ppm	Community Air Qual. Guides--1969[7]

This is no small task, if the special needs of the recreational diver, the ship's hull inspector, the underwater demolition team expert, the hard-hat diver, and aquatic habitat saturation diver are to be supported. Not only must the physiological and pathological consequences of exceeding the set limits be considered, but circumstance and duration of exposure must be established. Failure to do so may result in a definite hazard to the individual diver on the one hand, or, on the other, excessive cost in complying with unnecessarily restrictive limitations, with the possibility of an otherwise feasible project.

In any attempt to assess rational limits for the Navy, it is first necessary to review some of the sources of carbon monoxide to which the man is subjected. Some of these are outlined in Table II. The importance of cigarette smoke and internal combustion engine exhaust fumes as ubiquitous sources of carbon monoxide cannot be overemphasized.

Table II. - Carbon Monoxide and the Environment

Atmosphere Level	%HbCO	References
Body Metabolism	1.64	McIlvaine 1969
	0.4	Landlaw 1969
	0.80-3.61	Luomanmaki 1969
		Goldsmith
Cigarette Smoking	3-3.80	McIlvaine 1969
Light 400 ppm	3.8	Goldsmith Cohen 1969
Heavy	6.9	Goldsmith Cohen 1969
City Traffic		
Sweden	0.4-1.1	Goethe 1969
New York 13 ppm		Bove' 1970
Chicago 0-44 ppm		Landau 1969
Parking Garage 59 ppm	7	Ramsey 1967

Hemoglobin metabolism as a source of carbon monoxide has only recently attained prominent recognition (Goldsmith and Landlaw 1968[12], Landlaw 1969)[15].

With an understanding of the sources of carbon monoxide, it is next necessary to review its biological effects. Without much question, the key mechanism in the pathogenesis of carbon monoxide toxicity is the tenacious bond that it forms with the heme group of the hemoglobin molecule (Root 1965[20], Goldsmith 1968[11]). This bond competes for the position required for effective oxygen and carbon dioxide transport. Depending on the fraction of carboxyhemoglobin effectively unavailable for these vital functions, relative or absolute tissue hypoxia occurs. There is in addition an indirect effect on the remaining oxygen-hemoglobin bonds, which impedes release of oxygen to the capillary-tissue level. The resulting non-availability of hemoglobin sites for carbon dioxide removal serves not only to enhance tissue hypoxia, but also is most likely responsible for headaches which are frequently seen with prolonged exposure to low levels of carbon monoxide (100 ppm). It is considered that the level of saturation of hemoglobin with carbon monoxide is a function of not only ambient partial pressure of this gas, but also the partial pressure of oxygen, (West 1966[24]). The effect on the equilibrium constant of pressure and temperature have been investigated (Rodkey 1969[21]) and for the purposes of this discussion are considered to be negligible. The major pathway of excretion is via the lungs, without chemical change. An average of 0.16% per hour is, however, oxidized to CO_2 (Luomanmaki 1969).[16]

Table III. - Carbon Monoxide Acute Effects - Duration of Exposure 1 hour

Atmosphere Level ppm	%HbCO	Effect	References
400	7.2	Nil	Sax 1957
800	14.4	Headache	Gleason 1957
		Breathlessness with exertion	Forbes 1945
1600	29	Confusion Collapse on exertion	
3200	58	Unconsciousness	
4000	72	Profound coma	
4500	81	Immediate death	

The acute effects of carbon monoxide, together with associated atmospheric and hemoglobin saturation levels are listed in Table III. It is of particular note that exposure resulting in carboxyhemoglobin levels less than 29% are compatible with a conscious state, albeit a confused one. Evidence has been developed by several workers that considerably lower limits than these might be associated with impairment of the special senses and perhaps cognitative defects (see Table IV). The

Table IV. - Carbon Monoxide Low Level Effects

Effect	Inspired Air Conc	References
Visual Threshold	5%	McFarland 1944
Psychomotor Tests	2%	Schulte 1963
Time Discrimination	50 ppm	Beard 1967
Athero-sclerosis Rabbits	250-350 ppm	Astrup 1966

issue of chronic effects has not yet been resolved. In at least one animal model, predisposition to atheroma formation is enhanced by exposure to carbon monoxide. Although clear-cut chronic effects have never been unequivocally demonstrated in man, in 1965, the tentative halving of the threshold limit for carbon monoxide (from 100 ppm to 50 ppm) for an eight-hour day forty-hour week exposure (American Conference of Government Industrial Hygienists 1959, 1968)[1] (Hygienic Guides Carbon Monoxide 1965)[13] has been recommended.

With an assemblage of exposure sources, biological effects, and background body burden, it is possible to approach more directly a limit or limits that are applicable to the diver. Some of the questions that must be answered in so doing are included in the following list:

a. How important are the chronic effects in relationship to the exposure level and duration?

b. How important is optimum performance of special senses to the accomplishment of the particular diving mission?

c. How are the proposed limits related to self-pollution by cigarette smoking body burden? Would it be desirable to raise limits, if such could be accomplished by excluding cigarette smokers from the mission or project?

d. Might an artifically high limit effectively eliminate the use of highly desirable system (such as deep submarine escape) because of associated cost, weight, and space considerations?

It is considered that the resolution of these and similar questions requires, first of all, close communication between the user and his medical advisor, with both parties being familiar, in at least a general way, with operational and biomedical constraints. The approach of adopting a limit that is universally applicable is seriously questioned.

Let us first consider saturation exposure in a sub-aquatic habitat. Table V illustrates some of the interrelationships between environmental pressure, oxygen partial pressure, and various levels of atmospheric contamination by carbon monoxide. It is assumed, for purposes of constructing the table, that equilibrium has been achieved, that the atmospheric concentration of carbon monoxide has been generated at ambient pressure, that arterial tension of carbon monoxide approximates atmospheric partial pressure, and that ambient partial pressures of oxygen are sufficient to result in arterial levels of 150 mmHg and 300 mmHg respectively. Equations derived from (West 1966[24]) were used for the calculations. It can be seen that for currently accepted threshold limits of 20 ppm (BuMed 1968)[6] that for depths less than 400 feet the margin of safety (from acute effects) is quite high, but that for 800 feet (a depth within operational reach) an unacceptable carboxythemoglobin concentration will be built up. Further, at lesser pressures, sea level or two atmospheres absolute, atmospheric concentrations of 100 ppm in non-smokers should result in minimal symptomatology. Increasing arterial oxygen tensions to 300 mmHg (a relatively safe maneuver from the point of view of cerebral and pulmonary oxygen toxicity) reduces the hazard of concentrations of carbon monoxide of 100 ppm still further when near the surface, without appreciably affecting the hazard at 800 feet. This then, is an example of circumstances in which a single arbitrary threshold limit value has limited usefulness.

At the opposite end of the spectrum are the requirements for gas purity for submarine escape. Admittedly, the escapee is, at best, a modified diver. However, many of the problems with which he must cope are qualitatively similar to those of divers, particularly with respect to the required degree of purity of the gas he must breathe.

It is within the state of the art to provide the submarine service with an escape

Table V. - Saturation Exposure to Carbon Monoxide Implications of Environmental Pressure and Oxygen Partial Pressure

Depth Atmosphere	Feet	$\overline{\text{mmHg}}$	CO ppm ambient	P_{CO}	P_{O_2}	$\overline{\%\text{HbCO}}$
1	SL	760	100	0.076	150	9.6
2	33	1520	100	0.15	150	17.35
13	400	9900	100	0.99	150	58
25	800	19000	100	1.90	150	72
1	SL	760	50	0.038	150	5.05
2	33	1520	50	0.075	150	9.5
13	400	9900	50	0.50	150	41
25	800	19000	50	0.95	150	57
1	SL	760	20	0.015	150	2.03
2	33	1520	20	0.03	150	4.02
13	400	9900	20	0.20	150	21.9
25	800	19000	20	0.38	150	34.8
1	SL	760	100	0.076	300	5.3
2	33	1520	100	0.15	300	9.5
13	400	9900	100	0.99	300	41
25	800	19000	100	1.90	300	57
1	SL	760	50	0.038	300	2.6
2	33	1520	50	0.075	300	5.0
13	400	9900	50	0.50	300	26
25	800	19000	50	0.95	300	40
1	SL	760	20	0.015	300	1
2	33	1520	20	0.03	300	2.06
13	400	9900	20	0.20	300	12.4
25	800	19000	20	0.38	300	21

$$\frac{HbCO}{HbCO + HbO_2} = \frac{KpCO}{PO_2 + KpCO}$$

SL = Sea Level

system requiring minimal active participation of the individual escapee. Substantial savings would thus be made in escape trunk size, weight, and complexity. With this system there would be provision for reaching the surface. In developmental consideration of this system, the question of the purity of the breathing gas arises in the context of the requirements for special "ultra clean" gas. In the situation in which exposure time is short (in the order of magnitude of 1-2 minutes), and cooperation of the individual escapee is not required, it would appear that contamination of the breathing gas with carbon monoxide could and should be tolerated up to a point approaching a percentage that would cause mental confusion (%HbCO - 29). Using the equations developed by Forbes[8], times in minutes have been calculated for achieving this level for various atmospheric concentrations of carbon monoxide (Table VI) at environmental pressures of one atmosphere. In Table VII, an attempt has been made to extrapolate the times under pressures equivalent to 400 and 100 feet of sea water. The partial pressures of carbon monoxide have been calculated for a number of assumed concentrations of carbon monoxide at the respective depths. These partial pressures have been translated to a surface equivalent concentration of carbon monoxide by dividing by 760 mmHg (sea level pressure) and times calculated by the equations of Forbes[8]. It can be seen that an atmosphere as foul as 1500 ppm CO can be breathed for five minutes at 400 feet before a carboxyhemoglobin level of 30% is reached. It is entirely possible that this is sufficient time for a successful escape. The verification and availability of such information, it would seem, would be of value not only in the design of future submarine escape systems, but also to the captain of a disabled submarine. To exclude the option of individual escape simply because of minimal or even moderate fouling of the breathing gas with carbon monoxide on the bases of established limits of 20 ppm would appear in these contexts to be misguided.

It is readily apparent and indeed must be clearly pointed out that there is a paucity of data bearing on the reaction of man to carbon monoxide under elevated environmental pressures. The role of contaminant gas partial pressure relationship to symptomatology has not been either completely defined or verified. The time function for the reaction in a hyperbaric environment likewise is currently only a matter of speculation. The interrelationships of elevated tensions of carbon dioxide to various levels of carbon monoxide have yet to be carefully explored. The involvement of other biochemical systems, such as the cytochrome systems and the impact of carbon monoxide effects on the special senses in the presence of inert gas narcosis are all fertile areas demanding investigation prior to assurance of applicability of threshold limits to divers breathing gas. Much of this work can be carried out, at least initially, by the use of animal models. It should be remembered, however, that epidemiological techniques and involvement of operationally experienced biomedical personnel are essential if limits that are relevant to operational needs are to be provided to the diving community.

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ADDENDUM FOR REPORT NO. 629

Page 6, line 6, Insert after the word 'for' the words 'thermal protection upon', so that the sentence will read:

"With this system there would be provision for thermal protection upon reaching the surface."

Table VI. - Concentration Relationships for Acceptable End Point of Confusion/Collapse on Exertion %HbCO = 30 Sea Level

T(min)	%CO	ppm
0.5	20	$2X10^5$
1	10	$1X10^5$
10	1	10^4
30	.33	3300
60	.17	1700

%HbCO = 3X%COXt Forbes 1945

Table VII. - Projected Time at Selected Depths for Acceptable End Point of Confusion/Collapse on Exertion %HbCO = 30

Depth	Ambient	Pco	Surface Equivalent	Time in min. to develop
	CO ppm	mmHg	%CO $Pco/760^{X100}$	30%HbCO*
400 feet	20	0.2	0.026%	380
10^4 mmHg absolute	50	0.5	0.066%	152
	100	1	0.13%	77
	500	5	0.66%	15
	1000	10	1.3%	8
	1500	15	2%	5
100 feet	500	1.52	0.2%	50
3040 mmHg absolute	1000	3.04	0.4%	25

* %HbCO = 3X % COXt Forbes 1945